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PIEZOELECTRIC CERAMIC COMPOSITIONS

Abstract:

Abstract of GB1263780

1,263,780. Piezo-electric ceramics. MATSUSHITA ELECTRIC INDUSTRIAL CO. Ltd. 13 May, 1969, No.24358/69,. Heading G1J. A piezo-electric ceramic composition consists of a solid solution of a material defined by the area ABCDEF of Fig. 2 and further containing 0À1 to 5 weight per cent of manganese dioxide.

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DRAWINGS ATTACHED

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(54) PIEZOELECTRIC CERAMIC COMPOSITIONS

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED, a Japanese company of Kadoma, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to ceramic materials which have or can be given piezoelectric properties, and to articles manufactured from such materials. As will appear in more detail hereinafter, the invention relates to ferroelectric ceramics which are in the nature of polycrystalline aggregates of certain constituents.

At the present time, there is a wide use of piezoelectric materials in transducers, for the production, measurement and sensing of sound, shock, vibration, pressure and other quantities which can be imposed upon the piezoelectric material as mechanical strain. The desirable characteristics of a piezoelectric varies with the particular use to which the material is to be put. For example, electromechanical transducers such as gramophone pickups and microphones require materials having a high electromechanical coupling coefficient and high dielectric constant. On the other hand, in primarily resonant applications, such as in filter devices, it is desirable that the material should have a high value of mechanical quality factor, or mechanical Q, and a high electromechanical coupling coefficient. In general, the characteristics of piezoelectric materials should have good stability with respect to both temperature and time.

The present invention is concerned with the production of piezoelectric materials which are improved in one or more of the respects mentioned, and the invention includes a ceramic composition comprising a solid solution consisting of a material comprising the systems

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbTiO_3\text{-}PbZrO_3,$$

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbTiO_3 \text{ or}$$

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbZrO_3,$$

selected from the area bounded by lines connecting points A,B,C,D,E and F as defined below, modified by the addition of manganese dioxide (MnO_2) in a proportion of 0.1 to 5 percent by weight.

A preferred composition comprises a solid solution consisting of a material selected from the area bounded by lines connecting points G, H, I, J, K and L as defined below and containing a quantity of manganese equivalent to 0.2 to 3 percent by weight of manganese dioxide (MnO_2).

A further preferred composition comprises a solid solution consisting of a material selected from the area bounded by lines connecting points M, N, O, P and Q as defined below and containing a quantity of manganese equivalent to from 0.2 to 3 percent by weight of manganese dioxide (MnO_2).

Preferred features and advantages of the invention will appear from the following description of embodiments of the invention, given by way of example, in conjunction with the accompanying drawings, in which:—

Figure 1 is a diagrammatic cross-sectional view of a simple piezoelectric body; and

Figure 2 is a triangular composition diagram.

Figure 1 shows diagrammatically the construction of a simple piezoelectric body, which can form the active element of an electromechanical transducer. This element has as its active member a body 1 of piezoelectric ceramic material. The body of material may have any suitable shape, but conveniently may be in the form of a thin disc or wafer.

The body 1 is provided on its two major parallel surfaces with electrodes 2 and 3 and conductive leads 5 and 6 are fastened to the electrodes 2 and 3, for example by means of solder at 4. The body of material is initially polarised, and when the body is subjected to mechanical stress, such as shock, vibration or other applied mechanical force, an electrical voltage is developed at the electrodes 2 and 3, and the voltage fed to an external load device, over leads 5 and 6. The action is reversible, and if an electrical voltage is applied to electrodes 2 and 3, the ceramic body will be

mechanically deformed. It is to be understood that for the purposes of the present specification, the expression electromechanical transducer is to be taken in its broad sense, and includes uses of the piezoelectric material in circumstances where there is an interchange of electrical and mechanical energy, such as piezoelectric filters, frequency control devices and the like. Such materials can also be adapted for use to other applications, requiring materials having dielectric, piezoelectric and/or electrostrictive properties.

The ceramic body of the transducer is formed of a composition of material which is a polycrystalline ceramic,

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbTiO_3\text{-}PbZrO_3,$$

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbTiO_3 \text{ or}$$

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbZrO_3.$$

It has been found that within certain ranges of proportions, these materials, with appropriate additions of MnO_2 can be polarised to yield piezoelectric bodies which have a high mechanical quality factor, and high electromechanical coupling coefficients. The bodies show good stability of resistance at resonance and of quality factor (Q_M) with time.

The triangular composition diagram of Figure 2 includes all compositions coming within the ternary system

$$Pb(Li_{1/4}Nb_{3/4})O_3\text{-}PbTiO_3\text{-}PbZrO_3,$$

but some of the compositions included within the diagram do not exhibit any substantial degree of piezoelectric properties, and many are mechanically active only to a small degree. For convenience, the planar coupling coefficient (K_p) of test discs of the material will be taken for the purpose of comparing piezoelectric activity. Thus, all materials having a composition which lies within the area bounded by lines connecting the points A, B, C, D, E and F in Figure 2, after polarisation, showed a planar coupling coefficient of approximately 0.10 or greater. Materials having a composition lying within the area bounded by lines connecting points G, H, I, J, K and L in Figure 2 exhibited after polarisation a planar coupling coefficient of about 0.3 or greater. Materials having a composition lying within the area bounded by lines joining points M, N, O, P and Q after polarisation, showed a planar coupling coefficient of about 0.50 or greater.

The points A to Q are defined in the following Table I in terms of molar percentages of the three components of the ternary system.

TABLE I

	Composition		
Point	$Pb(Li_{1/4}Nb_{3/4})O_3$	$PbTiO_3$	$PbZrO_3$
A	37.5	62.5	—
B	25.0	75.0	—
C	1.0	75.0	24.0
D	1.0	11.5	87.5
E	12.5	—	87.5
F	37.5	—	62.5
G	35.0	40.0	25.0
H	10.0	65.0	25.0
I	1.0	56.0	43.0
J	1.0	39.0	60.0
K	10.0	25.0	65.0
L	35.0	25.0	40.0
M	25.0	37.5	37.5
N	10.0	49.0	41.0
O	3.0	49.0	48.0
P	3.0	43.0	54.0
Q	8.5	37.5	54.0

Compositions described herein can be prepared by suitable known ceramic production methods but a preferred method, described in more detail hereinafter, involves the use of PbO or Pb_3O_4, Li_2CO_3 or $LiOH.H_2O$, Nb_2O_5, TiO_2, ZrO_2, and MnO_2.

The starting materials, consisting of lead oxide (PbO), lithium carbonate (Li_2CO_3), niobia (Nb_2O_5), titania (TiO_2), zirconia (ZrO_2) and MnO_2, all of relatively pure grade, such as that available as commercially pure grade, are intimately mixed, with added distilled water, in a rubber lined ball mill. In milling the mixture, care has to be observed to avoid contamination of the mixture by wear of the milling ball or stones, or the proportions of the ingredients must be varied to compensate for such wear, if possible.

Following wet milling, the mixture is dried and then mixed in order to ensure a mixture as homogeneous as possible. The mixture is then formed into suitable shapes, by compacting under pressure; a suitable pressure is 400 kilograms per square centimetre. The compacted bodies are then pre-reacted by calcining at a temperature of approximately 850°C for two hours.

After calcining, the reacted material is allowed to cool and is then wet milled to bring it to a small particle size. The MnO_2 can be added after calcining the other starting materials, in which case also the reacted material, with the added MnO_2, must be milled to a small particle size. In this milling also it is necessary to exercise care to avoid contamination by wear of the milling balls or stones, or to vary the proportions of the ingredients to compensate for such wear. The material is then formed into a mix or slip suitable for pressing, slip casting or extruding,

as may be desired in accordance with conventional ceramic production methods, and into such shapes as may be desired.

Samples of the material were prepared. These samples were made by adding to 100 grams of the milled pre-sintered mixture 5 ccs of distilled water. The mix was then used to produce, by pressure, discs 20 mm in diameter and 2 mm thickness, using a pressure of 700 kg/cm². The pressed discs were fired at a temperature of 1200° to 1280°C for 45 minutes.

In contrast with the firing, for sintering, of lead compound such as lead titanate zirconate, it is an advantage of the materials described that there is, in firing, a relatively small loss of PbO by evaporation. Accordingly, it is not necessary to fire the composition in an atmosphere of PbO, nor is it necessary to take special care to observe a predetermined temperature gradient in the furnace, as is the case with certain materials of the prior art. For the purpose of the present invention, satisfactory results have been obtained merely by heating the samples in a crucible of alumina, with a cover of the same material.

After firing, the sintered ceramic discs are polished on their major surfaces, when the discs will have been reduced to a thickness of 1 mm. The polished surfaces of the disc are then coated with a suitable silver paint and fired to form silver electrodes on the surfaces. The discs are polarised; they are immersed in a bath of silicone oil at 100°C, a unidirectional voltage gradient of 4 Kv per mm is maintained for one hour, after which the discs are field-cooled to room temperature, through a period of thirty minutes.

The piezoelectric and dielectric properties of the polarized specimens were measured at 20°C in a relative humidity of 50 percent, at a frequency of 1 kHz. Example of materials made and polarized in this way, together with relevant details of electromechanical and dielectric properties, are given in Table II below. In this Table the various constants and coefficients are as follows:

ε = Dielectric constant
K_p: planar piezoelectric coupling coefficient
Q_M: mechanical quality factor.

The electrical characteristics given are as measured 24 hours after polarisation.

TABLE II

Example No.	Basic Composition (Mol percent)			MnO_2 (Percent by Weight)	ε	K_p	Q_M
	$Pb(Li_{1/4}Nb_{3/4})O_3$	$PbTiO_3$	$PbZrO_3$				
1	3.0	46.0	51.0	0.5	752	0.53	564
2	6.0	46.0	48.0	0.5	1237	0.60	2230
3	12.5	50.0	37.5	0.5	786	0.37	2540
4	12.5	43.5	44.0	0.2	1440	0.45	1425
5	12.5	43.5	44.0	1.0	995	0.55	1626
6	12.5	43.5	44.0	3.0	576	0.50	1402
7	12.5	37.5	50.0	0.5	743	0.52	1348
8	25.0	37.5	37.5	0.5	1523	0.52	873

Table III gives the temperature coefficient of mechanical Q_M and of the resonant frequency f_r of the eight samples as set out in Table II in the temperature range of 20—80°C.

TABLE III

Example No.	Temperature Coefficient	
	Q_M	f_r
1	13.3	0.107
2	20.1	0.216
3	5.7	0.039
4	10.3	0.095
5	15.2	0.122
6	12.9	0.154
7	18.8	0.205
8	22.6	0.261

It will be evident from Table III that the samples given show good stability of resonant frequency in the temperature range specified, and that the mechanical quality factor Q_M is also stable in this range.

These properties are important when the piezoelectric materials are used in piezoelectric transformers and filters. The term piezoelectric transformer is intended to include passive electrical energy transfer devices or transducers employing the piezoelectric properties of a material in the transformation of voltage, current or impedance. For these applications of the ceramics the piezoelectric materials should have a high mechanical quality factor and high electromechanical coupling coefficient and good stability of resonant frequency and mechanical quality factor with temperature. In the case of a piezoelectric transformer used, for example, in a television receiver, a suitable piezoelectric material is necessary to ensure stability, with temperature, of the output current and voltage. The materials described have properties which make them suitable for use in electromechanical transducers in gramophone pick-ups, microphones and voltage generators for ignition systems, though these are not the only uses of the materials. Materials suitable for other uses can also be obtained by selection from the possible range of materials.

Compositions containing more than 5 percent by weight of MnO_2 have a relatively low mechanical quality factor and planar coupling coefficient. Compositions containing less than 1 percent by weight of MnO_2 have a relatively low mechanical quality factor.

Ceramic materials of the compositions described are of good physical quality and polarize well.

WHAT WE CLAIM IS:—

1. A ceramic composition comprising a solid solution consisting of a material selected from the area bounded by lines connecting points A, B, C, D, E and F as defined herein, and containing a quantity of manganese equivalent to 0.1 to 5 percent by weight of manganese dioxide (MnO_2).

2. A ceramic composition comprising a solid solution consisting of a material selected from the area bounded by lines connecting points G, H, I, J, K and L as defined herein and containing a quantity of manganese equivalent to 0.2 to 3 percent by weight of manganese dioxide (MnO_2).

3. A ceramic composition comprising a solid solution consisting of a material selected from the area bounded by lines connecting points M, N, O, P and Q as defined herein and containing a quantity of manganese equivalent to from 0.2 to 3 percent by weight of manganese dioxide (MnO_2).

4. A piezoelectric ceramic material consisting of the solid solution having the formula:

$$Pb(Li_{1/4}Nb_{3/4})_{0.125}Ti_{0.435}Zr_{0.440}O_3$$

and further containing 1.0 percent by weight of manganese dioxide (MnO_2).

5. A piezoelectric ceramic material consisting of the solid solution having the formula:

$$Pb(Li_{1/4}Nb_{3/4})_{0.060}Ti_{0.460}Zr_{0.480}O_3$$

and further containing 0.5 percent by weight of manganese dioxide (MnO_2).

6. An improved ceramic material in accordance with any of the Examples of Table II herein.

7. An improved ceramic material according to claim 1 and substantaily as described with reference to the accompanying drawings.

8. A piezoelectric ceramic body of material having a composition in accordance with any of the preceding claims.

9. A device including as an active element a piezoelectric body in accordance with claim 8.

10. An improved process for the manufacture of ceramic materials according to claim 1 and substantially as described with reference to the accompanying drawings.

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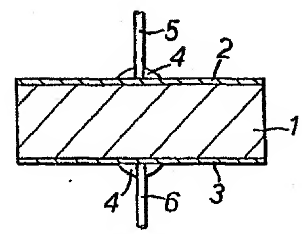
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FIG. 1.

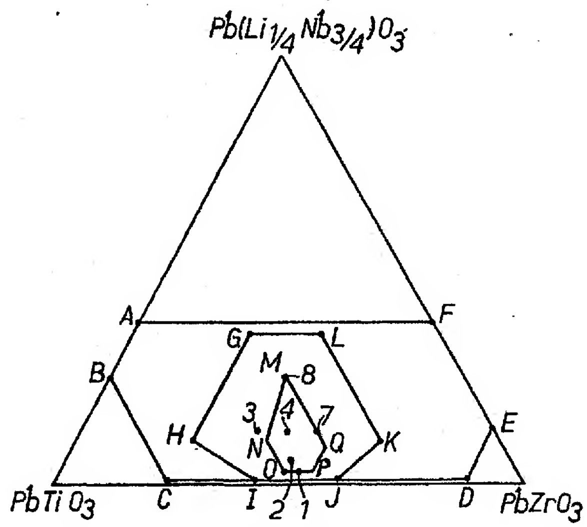
Pb(Li1/4 Nb3/4)O3
A
F
G
L
M
8
B
3
4
7
H
N
Q
K
E
O
P
PbTiO3
C
I
2
1
J
D
PbZrO3

FIG. 2.